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PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

Thermoplastic Composition

We, EASTMAN KODAK COMPANY, a Company organized under the Laws of the State of New Jersey, United States of America of 343 State Street, Rochester, New York 14650, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a thermoplastic composition and its use as a coating composition.

In the preparation of coated substrates, or the coating of articles whether they be mounted on substrates or not, the process of hot melt coating is highly advantageous. A particular desirable process for applying such coatings is a curtain coating process in which a falling curtain of a molten, viscous, thermoplastic material is applied to a substrate or an article by passing that substrate or article through the falling curtain and thereby causing a coating to be applied to the upwardly facing surfaces of the substrate or the article.

The ultimate use of the coated substrate or article, as well as the process conditions for coating that substrate or article, dictate that the thermoplastic coating composition have a particular set of properties. The final coating must be transparent, tough, strong, tear resistant, and economical. In the melt, this composition must be sufficiently viscous to form a continuous falling film without rupturing and must have sufficient heat stability to be maintained in a molten condition without degradation over processing times.

Those materials known in the past that satisfy these conditions are the plasticized cellulose esters. Although cellulose esters are highly desirable curtain coating compositions they suffer from two weaknesses which cause cellulose esters to be unacceptable as coating materials in certain end-use applications. Cellulose esters have relatively poor barrier properties, i.e. moisture and air diffuse to some extent through cellulose esters, and they also tend to adhere too tightly to certain substrates and articles.

Unmodified polyethylene is known to have good barrier properties but this material is not suitable as a curtain coating resin because it tends to cross-link and to produce gel specks which cause the final coating to be commercially unacceptable. Ethylene copolymers have, for several reasons, not been entirely suitable for a curtain coating process. In particular they have cross-linked and solidified in the curtain coating machine.

It has now been found that blends of certain ethylene copolymers with certain polyolefins can be employed advantageously to provide a thermoplastic composition having a combination of properties which is admirably suited for coating, e.g. for the curtain coating process.

According to the present invention, there is provided a thermoplastic composition having a melt viscosity at 190°C. of 5,000 to 125,000 cp. comprising:

(1) 40 to 99% by weight of a copolymer of 55 to 99% by weight of ethylene and 1 to 45% by weight of at least one comonomer comprising:

(a) an alkenyl alkanoate wherein the alkenyl portion contains 2 to 4 carbon atoms and the alkanoate portion contains 2 to 6 carbon atoms,

(b) an alkyl acrylate wherein the alkyl group contains 1 to 8 carbon atoms,

(c) an alkyl methacrylate wherein the alkyl group contains 1 to 8 carbon atoms,
(d) acrylic acid, or
(e) methacrylic acid, and
(2) 1 to 60% by weight of a crystallizable polymer comprising a homopolymer or copolymer of an α-olefin having 2 to 10 carbon atoms, said polymer having a melt viscosity at 190°C. of 1,000 to 20,000 cp. when polyethylene is used and 1,000 to 400,000 cp. when a homopolymer or copolymer of propylene or a higher α-olefin is used.

Thermoplastic compositions in accordance with the present invention have excellent barrier properties, and are particularly suitable for packaging food materials. They have a high melt stability.

In preferred embodiments of this invention, the melt viscosity at 190°C. of the coating composition is at least 15,000 cp. and the copolymer is ethylene/vinyl acetate. An especially desirable combination is a thermoplastic composition comprising about 80—95% of a copolymer of ethylene and vinyl acetate in which 70—85% by weight of the copolymer is derived from ethylene and the remaining 15 to 30% is derived from vinyl acetate.

Thermoplastic compositions in accordance with the present invention are suitable for use in any process in which the coating composition is heated or otherwise formed into a molten viscous mass, and while in that condition, is applied as a coating to a substrate or article and permitted to congeal in place. In one of such processes, the hot molten composition is applied to a roller which in turn applies the molten composition to a flat substrate.

Among the most versatile of such processes, however, is that which is known as the curtain coating process in which a hot melt is extruded from a narrow slit-like orifice and permitted to fall vertically in the form of a molten viscous curtain. A substrate, an article, or the combination of an article on a substrate is passed horizontally through the falling curtain, causing the curtain to drape itself over the upwardly facing surfaces of the object to be coated. Alternatively, the molten curtain may be caused to move over the substrate, article or the combination of an article on a substrate which is held in a stationary position.

In certain instances, it may be advantageous to employ a vacuum to remove the air between the article or substrate being coated and the coating itself. The vacuum helps to produce a coating which conforms closely to the outer contour of the article or substrate, as well as removing oxygen and moisture which might otherwise corrode or be detrimental to the coated article or substrate. This feature of employing a vacuum is particularly advantageous when the coated object is either a porous substrate or a flat porous substrate with an article mounted thereon. Under these conditions a vacuum applied to the underneath side of the porous substrate while it is being passed through the falling curtain of molten thermoplastic material causes the curtain to deposit snugly over the surface of the flat substrate and the upwardly facing surfaces of any article mounted on the substrate. The coating composition of this invention advantageously has a melt viscosity at 190°C. of 5,000 to 125,000 cp., preferably at least 15,000 cp. and normally not greater than about 100,000 cp. The composition is essentially a blend of two types of components, one being an ethylene copolymer and the other being a poly(α-olefin).

The copolymer component is a copolymer of 55 to 99% by weight of ethylene and 1 to 45% by weight of any one or more of three types of esters and two types of acids. Preferably, the copolymer comprises 70 to 85% by weight of ethylene with the remaining 15 to 30% being derived from one or more of the other comonomers.

The comonomer may be:

(a) an alkenyl alkanoate in which the alkenyl portion contains 2—4 carbon atoms and the alkanoate portion contains 2—6 carbon atoms.
(b) an alkyl acrylate wherein the alkyl group contains 1—8 carbon atoms.
(c) an alkyl methacrylate wherein the alkyl group contains 1—8 carbon atoms,
(d) acrylic acid, or
(e) methacrylic acid.

Suitable alkenyl alkanoates include esters such as vinyl, isopropenyl, butenyl, isobutenyl, and allyl esters of alkanoic acids having 2 to 6 carbon atoms. Suitable alkanoic acids include acetic, propionic, butyric, valeric, and caproic acids and their isomeric derivatives, such as isobutyric, isovaleric, and isocaproic acids. Specific suitable alkenyl alkanoates are vinyl acetate, vinyl propionate, vinyl butyrate, vinyl valerate, vinyl caproate, isopropenyl acetate, butenyl acetate, isobutenyl acetate, isopropenyl butyrate, isopropenyl valerate, and allyl acetate.

Suitable alkyl acrylates and methacrylates include those acrylates and methacrylates in which the alkyl group contains 1—8 carbon atoms and is n-alkyl, isoalkyl, or other branched chain alkyl. Among such alkyl acrylates and methacrylates are: methyl, ethyl, propyl, isopropyl, isobutyl, amyl, isoamyl, hexyl, 2-ethylhexyl, heptyl, and octyl acrylates and methacrylates.

For the crystallizable polmer, ethylene and propylene homo- or copolymers are the preferred polyolefins, although other α-olefin polymers such as those derived from 1-butene,

1-pentene, 1-hexene, 1-heptene, 1-octene, 1-nonene, and 1-decene are also contemplated. The crystallizable polymer need not be a homopolymer but may be a copolymer such as, for example, a copolymer of ethylene and propylene, a copolymer of propylene and 1-butene, or a copolymer of ethylene and 1-butene.

The proportions of the two components of the thermoplastic composition according to this invention are such that 40 to 99% by weight of the final composition comprises the copolymer and 1 to 60% by weight of the final composition comprises the crystallizable polymer. It is preferred, however, that the copolymer comprise 80 to 95% by weight of the total composition with the crystallizable polymer comprising the remaining 5 to 20% by weight in order to provide the optimum combination of properties for most uses of the composition.

The thermoplastic composition in accordance with this invention may be used to coat substrates such as flat sheets, paper, cardboard, articles of any size, shape, or contour mounted on supporting substrates, such as toys mounted on a cardboard containing advertising or instructions for use of that toy, cosmetics mounted on a display support, and similar packages. It is furthermore contemplated that foods such as meat, fruit, vegetables and poultry may be packaged by encapsulation employing the composition in accordance with this invention by itself or in combination with a tray or other substrate to support the food. The composition forms a highly desirable encapsulation for dressed chickens or turkeys without the necessity of providing a supporting substrate.

Stabilizers normally added to protect the compositions during or after the coating operation against degradation by heat, light, or oxygen include dilauryl thiodipropionate (DLTDP), 2,6-ditertiary butyl-p-cresol (BHT), tris(nonylphenyl) phosphite (Polygard), dioctadecyl-p-cresol (DOPC), and 4,4'-thiobis-(6-tertiary butyl-m-cresol) (Santonox R), or various combinations of the compounds. Other phenolic or phosphite type stabilizers known to be effective for the stabilization of polyolefins may also be used in the stabilization of these compositions.

Although in most instances it will not be necessary nor appropriate to do so, the composition in accordance with this invention may have incorporated therein such substances as pigments, fillers, and decorative matter.

The invention will be more readily understood by reference to the following illustrative examples, in which all parts and percentages are by weight.

Example 1

A blend was prepared of 80% by weight of an ethylene/vinyl acetate copolymer and 20% by weight of a polyethylene. The copolymer comprised 82% by weight ethylene and 18% by weight vinyl acetate and exhibited a melt viscosity at 190°C. of 58,000 cp. The polyethylene had a melt viscosity at 190°C. of 4,000 cp. The melt viscosity of the blend was 34,000 cp. at 190°C.

Air-quenched films having a thickness of 5 mils were prepared with the assistance of a hot doctor blade on a flat casting surface. After the coating congealed, it was stripped from the surface and was found to have the following properties:

Tensile Modulus	6,000 psi
Tensile Yield Strength	700 psi
Tensile Break Strength	700 psi
Elongation	454%

Appearance — clear with slight haze.

Example 2

The blend described in Example 1 was mixed with melt stabilizers and used to coat various articles. The mixture comprised 400 parts by weight of the blend of Example 1, 1.5 parts of dilauryl thiodipropionate, and 1.5 parts of BHT.

This mixture was melt extruded into strands, quenched in water, and chopped into pellets to produce a homogeneous feed material for a curtain coating process. The pellets were melted and fed to the extrusion orifice of a curtain coating machine at a melt temperature of approximately 180°C. Toy motor vehicles mounted on porous paperboard were placed over a support beneath which a vacuum was applied. The falling curtain of molten material was moved across the above-described combination of toy motor vehicles, paperboard and vacuum support, causing the curtain to be deposited over the upwardly facing surfaces of the toys and the paperboard. Vacuum was then applied to draw the film down over the toys.

The congealed coating was clear and not tacky, and the resulting package was considered to be excellent. The coating operation was repeated continuously for two hours without any indication that the molten material was degrading or becoming unstable. The melt viscosity of the coating composition after two hours of operation was 45,000 cp. at 190°C.

Other items which were coated, some with and some without a supporting substrate, included whole dressed chickens, pieces of chicken, cheese, 1 lb. packages of bacon, screw drivers, door closers, baby bottle nipples, pencils, nuts and bolts, electrical components, transistor radio batteries, and pliers.

Films 7.5 mils thick were prepared from the above coating composition and had the following properties:

Tensile Break Strength (ASTM D882—61)	870 psi
Elongation (ASTM D882—61)	614%
Gloss (ASTM C3465—51)	60%
Timed Dart Impact at −40°C. (ASTM D758—48)	292g

EXAMPLE 3

A blend having a melt viscosity at 190°C. of 29,000 cp. was prepared comprising 80% by weight of an ethylene/vinyl acetate copolymer and 20% by weight of a polypropylene. The copolymer contained 82% by weight ethylene and 18% by weight vinyl acetate and had a melt viscosity at 190°C. of 58,000 cp. The polypropylene had a melt viscosity at 190°C. of 3,000 cp. This blend was stabilized with 0.1% DLTDP, 0.05% BHT, and 0.3% Polygard.

It was employed in a curtain coating process as described in Example 2, and performed very well. Air-quenched films, 5 mils thick, had the following properties:

Tensile Modulus	7,700 psi
Tensile Yield Strength	570 psi
Tensile Break Strength	570 psi
Elongation	58%

Appearance — clear with slight haze.

EXAMPLES 4—19

Blends of various proportions of copolymer compositions and polyolefins were prepared and employed in curtain coating operations as described in the preceding examples. In each instance the coatings were excellent. The blend proportions and properties are given in the following table.

Example	Copolymer		Polyolefin			
	Wt. %	Comonomer proportions Wt. percent	Wt. %	Type	Melt viscosity at 190°C. cp.	Melt viscosity of blend at 190°C. cp.
4	80	72 Ethylene 28 Vinyl Acetate	20	Polyethylene	3,800	42,000
5	80	95 Ethylene 5 Vinyl Acetate	20	Polyethylene	4,000	40,000
6	90	82 Ethylene 18 Vinyl Acetate	10	Polyethylene	4,000	50,000
7	85	85 Ethylene 15 Ethyl Acrylate	15	Polyethylene	4,000	45,000
8	80	88 Ethylene 12 Ethyl Acrylate	20	Polypropylene	75,000	60,000
9	50	82 Ethylene 18 Vinyl Acetate	50	Polypropylene	140,000	95,000
10	95	90 Ethylene 10 Isopropenyl Acetate	5	Poly(1-butene)	86,000	28,000
11	80	85 Ethylene 15 Isobutyl Acrylate	20	Copolymer: 60 Propylene 40 1-Butene	80,000	35,000
12	80	89 Ethylene 11 2-Ethylhexyl Acrylate	20	Polypropylene	60,000	50,000
13	80	92 Ethylene 8 Acrylic Acid	20	Polyethylene	10,000	40,000
14	98	85 Ethylene 15 Methyl Methacrylate	2	Polypropylene	100,000	24,000

Example	Copolymer		Polyolefin		Melt viscosity at 190°C. cp.	Melt viscosity of blend at 190°C. cp.
	Wt. %	Comonomer proportions Wt. percent	Wt. %	Type		
15	98	85 Ethylene 15 Methyl Methacrylate	2	Polypropylene	400,000	24,000
16	80	82 Ethylene 18 Vinyl Acetate	20	Copolymer: 97 Propylene 3 Ethylene	30,000	35,000
17	80	82 Ethylene 18 Vinyl Acetnte	20	Copolymer: 98 1-Butene 2 Ethylene	30,000	40,000
18	85	82 Ethylene 18 Vinyl Acetate	15	Polypropylene	380,000	82,000
19	80	90 Ethylene 10 Methacrylic Acid	20	Polypropylene	40,000	20,000
20	80	55 Ethylene 45 Vinyl Acetate	20	Polyethylene	4,000	41,000
21	80	82 Ethylene 18 Vinyl Caproate	20	Polypropylene	3,000	15,000
22	40	80 Ethylene 20 Vinyl Acetate	60	Polypropylene	50,000	54,000
23	99	75 Ethylene 25 Vinyl Acetate	1	Polypropylene	40,000	30,000
24	90	88 Ethylene 12 2-Ethylhexyl Methacrylate	10	Polypropylene	40,000	45,000
25	88	80 Ethylene 20 Methyl Acrylate	12	Polypropylene	20,000	60,000

WHAT WE CLAIM IS:—

1. A thermoplastic composition having a melt viscosity at 190°C. of 5,000 to 125,000 cp. and comprising:

(1) 40 to 99% by weight of a copolymer of 55 to 99% by weight of ethylene and 1 to 45% by weight of at least one comonomer comprising:
(a) an alkenyl alkanoate wherein the alkenyl portion contains 2 to 4 carbon atoms and the alkanoate portions contains 2 to 6 carbon atoms,
(b) an alkyl acrylate wherein the alkyl group contains 1 to 8 carbon atoms,
(c) an alkyl methacrylate wherein the alkyl group contains 1 to 8 carbon atoms,
(d) acrylic acid, or
(e) methacrylic acid, and

(2) 1 to 60% by weight of a crystallizable polymer comprising a homopolymer or copolymer of an α-olefin having 2 to 10 carbon atoms, said polymer having a melt viscosity at 190°C. of 1,000 to 20,000 cp. when polyethylene is used and 1,000 to 400,000 cp. when a homopolymer or copolymer of propylene or a higher α-olefin is used.

2. A composition as claimed in Claim 1, wherein the melt viscosity at 190°C. of the thermoplastic composition is at least 15,000 cp.

3. A composition as claimed in Claim 1 or 2, wherein the melt viscosity at 190°C. of the thermoplastic composition is not greater than 100,000 cp.

4. A composition as claimed in any one of the preceding Claims, comprising 80 to 95% by weight of the copolymer of ethylene and said at least one comonomer and 5 to 20% by weight of the crystallizable polymer.

5. A composition as claimed in any one of the preceding claims, wherein the copolymer of ethylene and said at least one comonomer comprises 70 to 85% by weight of ethylene and 15 to 30% by weight of said at least one comonomer.

6. A composition as claimed in any one of the preceding claims, wherein the crystallizable polymer is a polyethylene.

7. A composition as claimed in any one of Claims 1 to 5, wherein the crystallizable polymer is a polypropylene.

8. A composition as claimed in any one of Claims 2 to 7, wherein said at least one comonomer is vinyl acetate.

9. A composition as claimed in any one of Claims 4 to 8, comprising (1) 80 to 95% by weight of a copolymer of 70 to 85% by weight of ethylene and 15 to 30% by weight of vinyl acetate, and (2) 5 to 20% by weight of the crystallizable polymer.

10. A thermoplastic composition having a melt viscosity at 190°C. of 5,000 to 125,000 cp. and substantially as hereinbefore described.

11. A process of hot melt coating in which a thermoplastic coating composition is heated or otherwise formed into a molten viscous mass, and while in that condition is applied as a coating to an article, a substrate, or an article on a substrate, and permitted to congeal thereon, wherein the thermoplastic coating composition is a composition as claimed in any one of the preceding Claims.

12. A process for coating articles by forming a falling curtain of a viscous molten thermoplastic composition, causing an article to be passed through said curtain so as to deposit the curtain over the upwardly facing surface or surfaces of said article, and permitting the curtain to congeal in place, wherein the thermoplastic composition is a resinous material having a melt viscosity at 190°C. of 5,000 to 125,000 cp. and comprises:

(1) 40 to 99% by weight of a copolymer of 55 to 99% by weight of ethylene and 1 to 45% by weight of at least one comonomer comprising:
(a) an alkenyl alkanoate wherein the alkenyl portion contains 2 to 4 carbon atoms and the alkanoate portions contains 2 to 6 carbon atoms,
(b) an alkyl acrylate wherein the alkyl group contains 1 to 8 carbon atoms,
(c) an alkyl methacrylate wherein the alkyl group contains 1 to 8 carbon atoms,
(d) acrylic acid, or
(e) methacrylic acid, and
(2) 1 to 60% by weight of a crystallizable polymer comprising a homopolymer or copolymer of an α-olefin having 2 to 10 carbon atoms, said polymer having a melt viscosity at 190°C. of 1,000 to 20,000 cp. when polyethylene is used and 1,000 to 400,000 cp. when a homopolymer or copolymer of propylene or a higher α-olefin is used.

13. A process as claimed in Claim 12, wherein the article is supported on a substrate.

14. A process as claimed in Claim 13, wherein a vacuum is applied beneath the substrate to facilitate depositing the curtain.

15. A curtain coating process substantially as hereinbefore described in any one of the Examples.

16. A package comprising an article coated by a process as claimed in Claim 11.

17. A package as claimed in Claim 16, wherein the article is dressed poultry.

18. A package comprising an article coated by a process as claimed in any one of Claims 12 to 14.

19. A package as claimed in Claim 18, wherein the article is dressed poultry.

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